Nanocomposite Proton Conductors

Lutgard C. De Jonghe (Primary Contact),
Jeffrey A. Reimer, Philip N. Ross
Lawrence Berkeley National Laboratory
Materials Sciences Division
Berkeley CA 94720
Phone: (510) 496-6138; Fax: (510) 486-4881
E-mail: dejonghe@lbl.gov

DOE Program Officer: Refik Kortan
Phone: (301) 903-3308
E-mail: Refik.Kortan@Science.DOE.gov

Objectives

The program designs, synthesizes and tests rare earth phosphate materials for proton conducting applications in the temperature region of 300-450 degrees Celsius. The program relies on three major approaches: a theoretical understanding of proton conduction in rare earth phosphates employing quantum chemical computation and molecular simulation; the chemical design, synthesis, and proton conductivity measurement of nano-composite materials expected to exhibit facile proton conduction; and the structural and dynamical characterization of the nano-composite materials using a range of advanced characterization methods including nuclear magnetic resonance (NMR), high resolution TEM, and computational methods. The possibility of membrane forming-methods similar to those of the glass industry, and operation in the envisioned temperature range would offer considerable economic advantage for the hydrogen fuel cell technology.

Technical Barriers

Hydrogen fuel cells, using inorganic membranes, operating in the 300 to 450ºC range can offer significant practical advantages, such as lowered sensitivity to CO and other catalyst poisons, simpler thermal management, and low-cost electrocatalysis. However, no suitable oxygen ion or proton conductors exist below about 500ºC. These factors point to the necessity of exploring the feasibility of inorganic proton conductors capable of operating in a temperature range that is not accessible by polymer membrane fuel cells, and out of range for the solid oxide fuel cells. In addition, effective anode and cathode catalysis scenarios need to be developed as well.

Abstract

The program designs, synthesizes and tests rare earth phosphate materials for proton conducting applications in the temperature region of 300-450 degrees Celsius. The program relies on three major approaches: a theoretical understanding of proton conduction in rare earth phosphates employing quantum chemical computation and molecular simulation; the chemical design, synthesis, and proton conductivity measurement of nano-composite materials expected to exhibit facile proton conduction; and the structural and dynamical characterization of the nano-composite materials using a range of advanced characterization methods including nuclear magnetic resonance (NMR), high resolution TEM, and computational methods. Aliovalently-substituted rare earth phosphates and rare earth phosphate glasses are being synthesized and tested for proton conduction. A comparison of theoretical predictions and observed conductivities provides an insight into the microscopic nature of conduction and directs the synthesis of novel nano-composite rare earth phosphates with modified grain boundaries. Basic processes in effective, novel anodes and cathode composite electrodes are studied. The possibility of membrane forming-methods similar to those of the glass industry, and operation in the envisioned temperature range would offer considerable economic advantage for the hydrogen fuel cell technology.

Progress report

Synthesis and Characterization

Cerium phosphate nanoparticles with diameters of 10-180nm were synthesized by a variety of solution techniques. X-Ray Diffraction (XRD) determined the crystalline phase(s) present in each sample. Population, shift, and spin-lattice relaxation ^{31}P solid-state Nuclear Magnetic Resonance (NMR) measurements accounted for all the ^{31}P nuclei expected in each sample, and were able to distinguish between phosphorous nuclei in different environments and phases. Transmission Electron Microscopy (TEM) characterized the morphology and crystallinity of the powder samples as well as of the sintered compacts of the powders. In conjunction with TEM, Energy-Dispersive Spectroscopy (EDS) provided a measure of the composition of the bulk intergranular regions within each $CePO_4$ sample. The presence of an amorphous, phosphate-rich intergranular phase (*a*) was found in those samples prepared by dissolution of ceria in H_3PO_4 under various conditions.

Previously unrecognized amorphous grain boundary films are shown to provide rapid proton conduction paths in polycrystalline lanthanum phosphates. Experiments reveal the amorphous phosphorus-rich grain boundary films to be stable in air at 773 K, with a conductivity upwards of $2.5x10^{-3}$ S/cm at 773 K, many orders of magnitude higher than in the crystalline bulk. The results indicate the possibility of forming stable, high proton-conductivity nano-composites of RE-phosphate glasses and crystalline ceramics for intermediate temperature (573 K to 773 K) fuel cells. The results also indicate that it may be fruitful to explore doped, rare earth phosphate glasses as proton conductors.

Computational Modeling

Lanthanide phosphates are composed of non-connecting PO_4 tetrahedra and lanthanide ions. There are two types of transfer paths for protons: intra-tetrahedra and inter-tetrahedra. First-principles molecular dynamics calculations have been carried to investigate the proton transfer mechanisms in $LaPO_4$. The calculations are performed using pseudopotential plane-wave method, as implemented in VASP code. LCAO method (Linear Combinations of Atomic Orbitals) as implemented in SIESTA code is also used to verify the results.

Sr substituted RE-phosphates

In pure as well as aliovalently substituted cerium phosphate powder samples, the ^{31}P signal due to bulk monazite is observed to be paramagnetically shifted due to the electron on the Ce^{3+} ion.[1,2] A deconvolution of the ^{31}P NMR data obtained for 5% strontium substituted cerium phosphate reveals the presence of pyrophosphate species that are shifted upfield as a result of their proximity to the structural Ce^{3+} ions. This in turn is indicative of a successful substitution of cerium by strontium in the bulk monazite. The adsorbed phosphate species appear at ~ 0ppm, ostensibly far removed from structural cerium ions.

NMR studies
^{31}P NMR

Pure cerium phosphate

^{31}P NMR was employed to study pure and aliovalently substituted cerium phosphates. In pure, thermomechanically treated cerium phosphate samples with grain size $<$ 200nm, an extra peak, attributed to ^{31}P near the grain boundaries, is observed during Magic Angle Spinning (MAS) experiments. The intensity of this second peak increases proportionally to the surface area of the grain. All relevant ^{31}P NMR properties, shift, linewidth, T_1, and T_2 have been measured for the surface (when applicable) and bulk peaks in various phosphate samples.

Sr-substituted cerium phosphate – liquid state synthesis

Aliovalent substitution of cerium phosphates can be carried out via a solid state or a liquid state synthetic route. ^{31}P NMR was used to characterize the differences in the two methods of substitution. ^{31}P spectra of cerium (III) phosphates are characterized by a paramagnetic shift that originates from the unpaired electron on the Ce^{3+} ion and is propagated to neighboring nuclei as a function of the distance from the cerium ion.[1,2] The resulting shifts of the resonant ^{31}P frequency are large and can be used to identify the lattice phosphate signal. ^{31}P spectra for varying degrees of strontium substitution using the liquid synthetic route show the coexistence of the crystalline cerium phosphate grains and the amorphous intergranular boundaries. The formation of CeP_3O_9 is manifested as a broad peak centered at about -86 ppm. The broadening of the structural phosphate peak as a result of strontium substitution indicates the formation of crystalline pyrophosphate species and successful strontium substitution. Upon exceeding the natural solubility of strontium in cerium phosphates, the extra strontium assimilates in the intergranular boundaries. This is manifested as a shift of the resonance associated with the amorphous P-rich intergranular boundary towards values consistent with the chemical shifts of strontium pyrophosphate (-5, -7 ppm).

Sr substituted RE-phosphates - solid-state synthesis

In pure as well as aliovalently substituted cerium phosphate powder samples, the ^{31}P signal due to bulk monazite is observed to be paramagnetically shifted due to the electron on the Ce^{3+} ion.[1, 2] A deconvolution of the ^{31}P NMR data obtained for 5% strontium substituted cerium phosphate prepared via a solid state synthetic route reveals the presence of pyrophosphate species that are shifted upfield as a result of their proximity to the structural Ce^{3+} ions. This in turn is indicative of a successful substitution of cerium by strontium in the bulk monazite. The adsorbed phosphate species appear at ~ 0ppm, ostensibly far removed from structural cerium ions. Upon incremental substitution with strontium, the ^{31}P NMR spectra exhibit a buildup of adsorbed phosphate species at ~ 0ppm. This can be interpreted in terms of the finite solubility of strontium in cerium phosphates, beyond which any additional strontium phosphate assimilates into the intergranular boundaries. A comparison of the two synthetic routes indicates that the liquid state route results in larger adsorption of phosphates by the cerium phosphate grains and more P-rich boundaries. Similar studies were carried out on Lanthanum phosphates.

^{1}H NMR

One dimensional ^{1}H NMR spectra of strontium substituted, calcined lanthanum phosphate powders show one broad peak centered at ~ 5ppm. For strontium substituted lanthanum phosphate samples that have been calcined and exposed to steam, variable temperature NMR studies show that an increase in temperature results in the narrowing and a subsequent splitting of the broad peak into three resonances. The two peaks at 5 and 8 ppm are indicative of OH protons in the amorphous phosphate region, exhibiting varying degrees of bridging with other OH groups. Indeed ^{31}P NMR data for the same sample also indicates the formation of pyrophosphate species. The narrowing of the two peaks is a direct manifestation of thermal motion in the amorphous phases below 150°C and the corresponding linewidths can be used to calculate an activation energy of 0.134eV for proton conduction in this temperature regime. This value is consistent with previous studies involving hygroscopic polyphosphate composites[3].

Future directions

Synthesis and characterization

In the future, we will use our knowledge gained of the pure system to select appropriate secondary phases and dopants to enhance the conductivity. The next set of experiments involve doping with hypo- or hypervalent cations and anions, such as Sr^{2+} and SO_4^{2-}, which are expected to facilitate the incorporation and transport of protons within the microstructure. In addition, we plan to experiment with a different phase of pure $LaPO_4$ that uses protons to stabilize its structure.

Strontium Doping

Strontium has a valence of two and is thought to substitute for La^{3+} ions in the crystal structure, thereby leaving a (-1) local charge. This charge can be balanced by the presence of an H^+ ion, and in literature has shown to increase the proton conductivity of $LaPO_4$ with 5% addition of Sr by two orders of magnitude. In combination with our tailored processing we expect the addition of Sr to surpass reported conductivities at 500˚C for this material.

Composite with Second Phase

As noted, we have detected amorphous phases at grain boundaries of 'pure' $LaPO_4$. Based on our model, incorporating small amounts of phases with enhance proton conduction will increase conductivity to a large degree.

Hexagonal form of $LaPO_4$

The metastable hydrated hexagonal phase of $LaPO_4$ contains one hydrogen for every two La. This high degree of protonation is highly suggestive of excellent proton conduction, particularly along oxygen-lined tunnels along the c-axis of hexagonal grains. However, due to the conversion of hexagonal to unhydrated monoclinic phase of $LaPO_4$ at temperatures above 600˚C, it is difficult (or impossible) to form dense sintered pellets of hexagonal $LaPO_4$. Because the target range of operation of these membranes would be less than 500˚C, hexagonal $LaPO_4$ is a very intriguing option. To our knowledge, the creation of stable ceramic pellets of hexagonal $LaPO_4$ has not been attempted.

Based on results from hot pressed samples in our laboratory of monoclinic $LaPO_4$ at low temperature (<800˚C) and high pressure (>9,000 psi), we believe it may be possible to form sintered hexagonal $LaPO_4$. Future experiments will involve sintering of hexagonal $LaPO_4$ under special T and P conditions to avoid the formation of monoclinic $LaPO_4$. If successful, subsequent doping as mentioned above would have the potential to further enhance conductivity.

RE-glasses

The previous results indicate that substituted RE-glasses may also exhibit high proton conductivity. A range of Al-containing RE-glasses will be prepared, and a balance between high proton conductivity and high stability in the presence of water vapor will be sought.

NMR Studies

Extensive characterization of the site specific proton dynamics in the amorphous phosphate - rich intergranular phases of thermomechanically processed, aliovalently substituted lanthanum and cerium phosphates will be accomplished via a combination of variable temperature studies, relaxation measurements and two dimensional exchange experiments. The construction of a variable temperature ^{1}H probe with pulsed field gradient abilities is expected to afford an in-depth insight into the diffusion characteristics of protons at relevant temperatures. ^{31}P and ^{1}H NMR will be used to characterize the structure of rare earth phosphate glasses and the associated proton conduction characteristics.

Computational Modeling

The calculation work focuses on three aspects:

(a). Molecular dynamics calculations of proton transfer in an electric field. This would give continuous transfer paths.

(b). Quantitative analysis of the proton transfer barriers. This will provide information on the temperature dependence of proton transfer, and on the relative probabilities of the inter-tetrahedral transfers. Diffusion coefficients will then be computed and compared with H-NMR result and with proton conductivity measurements.

(c). The calculations will be extended to $CePO_4$ to determine the effects of the f electrons on proton transfer.

Electrodes and Electrocatalysis

A rapid screening method for perovskite-type cathode catalysts will be developed, and applied to candidates in the $Ln_{1-x}M_xM'O_3$ (Ln = lanthanide, M= alkaline earth, M' = transition metal) system.

Reaction paths and electrocatalytic processes in cathodes and anodes compatible with the proton-conducting electrolyte will be analyzed based on understanding and models that are developed.

DC and AC measurements in H2/Air cells will determine Electrochemical function of the anodes and cathodes.

Publications (including patents) acknowledging the grant or contract

1. L. Karpowich, S. Wilke, Rong Yu, G. Harley, J.A. Reimer, and L. C. De Jonghe, "Synthesis and characterization of mixed-morphology $CePO_4$ nanoparticles", LBNL- 62079 (2006)

2. Gabriel Harley, Rong Yu, and Lutgard C. De Jonghe, "Proton Transport Paths in Lanthanum Phosphate Electrolytes", LBNL-62080 (2006)

3. R. Yu, Q. Zhan, L.C. De Jonghe," Crystal structures and displacive transition in noble metal nitrides", LBNL-61998(2006).